880. *Polymeric Quinones. Part I. The Synthesis of Some Methylene-linked Di-, Tri-, and Poly-benzoquinones.*

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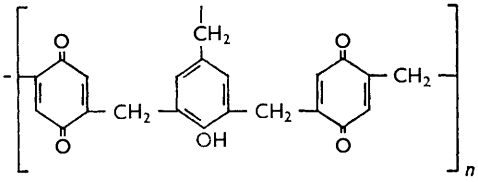
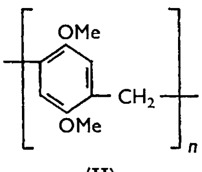
The syntheses of a number of novel dimeric and trimeric quinones, representing chain segments of two different polymeric quinones containing methylene bridges, are reported. The polyquinones were prepared from 1,4-di(chloromethyl)-2,5-dimethoxybenzene. The ultraviolet absorption spectra of the polymer segments are discussed.

POLYMERIC quinones have recently attracted study because of their potential application as oxidation–reduction resins [1] and their ability to behave as simple oxidoreductase models.[2] Practical applications of this type of polymer as diverse as anti-ulcer agents,[3] and as reagents for separation and identification of metals [4] and for the purification of saké have been reported.[5] Polymeric quinone structures are also known to occur naturally, for example, in the cell wall material of *Daldinia sporophores*.[6] Knowledge of the chemical, electrochemical, and physicochemical behaviour of such molecular arrays is still limited, and the work reported in this and the following paper [7] has been directed towards more fundamental knowledge of this type of system. Some details of the polymers and a preliminary account of this work have been reported elsewhere.[8]

The present work concerned two similar polymeric quinones. The first was prepared by oxidation of a 1 : 1 : 3 polycondensate (I) of quinol, phenol, and formaldehyde.[9] The second was prepared by polycondensation of equimolecular amounts of *p*-dimethoxybenzene and 1,4-di(chloromethyl)-2,5-dimethoxybenzene to give poly-(2,5-dimethoxy-1,4-phenylenemethylene) (II), which on demethylation and oxidation gave the corresponding polyquinone (III). Fractionation of the poly(dimethoxyphenylenemethylene) by solvent extraction showed it to be heterogeneous with respect to molecular weight: only small amounts were soluble in boiling benzene (4%), and boiling dimethylformamide (20%), the bulk (76%) being insoluble in boiling organic solvents; all three fractions gave correct analyses for structure (II), and the infrared absorption spectra of the three fractions were similar to one another and to that of the trimer (V; R = Me) described below. The soluble fractions are therefore considered to be polymers of lower molecular weight and of the same general structure; the insoluble fraction presumably is partially cross-linked.



(I)



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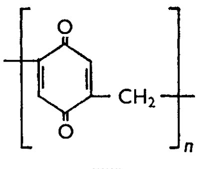

(III)

The sequence of reaction and the mechanism of the phenol–formaldehyde condensation and of the polycondensation of halogenomethylphenols have been much studied and

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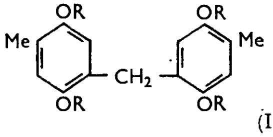
[1] Ezrin and Cassidy, *Ann. N.Y. Acad. Sci.*, 1953, **57**, 79; Lindsey, *Quart. Rev.*, 1962, to be published.
[2] Manecke, Bahr, and Reich, *Angew. Chem.*, 1959, **71**, 646.
[3] Ciba Ltd., B.P. 839,391/1957.
[4] Sansoni, *Angew. Chem.*, 1960, **72**, 587.
[5] Yamamoto, *Nippon Nogei-Kagaku Kaishi*, 1955, **29**, 838; *Chem. Abs.*, 1958, **52**, 20,772.
[6] Allport and Bu'Lock, *J.*, 1958, 4090.
[7] Lindsey, Peover, and Savill, following paper.
[8] Lindsey and Hunt, B.P. Appl. 15,583/1959; Hunt and Lindsey, *Chem. and Ind.*, 1961, 1272; Peover and Lindsey, *Chem. and Ind.*, 1961, 1273.
[9] Manecke, *Angew. Chem.*, 1955, **67**, 613.

discussed.[10] It is considered that in the polycondensation of 1,4-di(chloromethyl)-2,5-dimethoxybenzene with other aromatic groups in acetic acid described in the present paper the reaction must involve the more usual S_N1 type mechanism with formation of the corresponding carbonium ions as intermediates. Thus, in boiling acetic acid, in the absence of other reactants, quantitative conversion into the diacetate occurred with elimination of hydrogen chloride. In the presence of concentrated hydrochloric acid and after heating for three times as long, much of the di(chloromethyl) compound was recovered unchanged. The presence of an excess of chloride ions in the latter experiment had clearly shifted the ionisation equilibrium in the direction of the di(chloromethyl) compound. In the absence of an excess of hydrogen chloride and in the presence of reactive aromatic nuclei such as *p*-dimethoxybenzene, attack by carbonium ions leads to the formation of methylene bridges.[11]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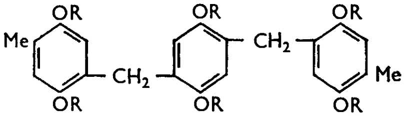
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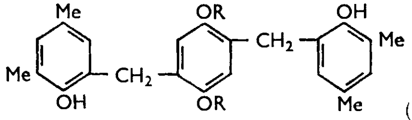
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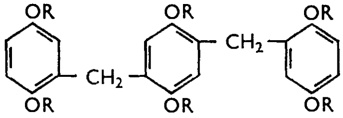
(VII)

Poly(dimethoxyphenylenemethylene) (II) was almost quantitatively demethylated by refluxing it with pyridinium chloride or hydriodic acid, as was confirmed in both cases by examination of the infrared spectra of the products and in the second case by measurement of the amount of methyl iodide liberated. However, a certain amount of structural " inactivation " of quinol groups occurred during the second procedure since polymers obtained in this way had much lower initial redox capacities than had polymers obtained by the first procedure.[7] The demethylated products were oxidised to the polyquinones by acidic ferric ammonium sulphate or by benzoquinone in boiling ethanol.

To aid the interpretation of the electrochemical behaviour of these polyquinone systems typical polymer chain segments were synthesised, notably compounds (IV—VI; R = Me); the first two of these corresponded to segments of the poly(dimethoxyphenylenemethylene), and the third was representative of polymer (I). A fourth compound, (VII; R = Me or H), was prepared for comparison.

The trimeric compounds (V—VII; R = Me) were prepared by condensing 1,4-di(chloromethyl)-2,5-dimethoxybenzene with, respectively, 1,4-dimethoxy-2-methylbenzene, 2,4-dimethylphenol, and *p*-dimethoxybenzene. The dimer (IV) was prepared by the known route [12] from 1,4-dimethoxy-2-methylbenzene and formaldehyde. All four compounds were smoothly demethylated with pyridinium chloride to the corresponding quinol derivatives (R = H), and the first three were conveniently oxidised to the corresponding quinones by refluxing them with benzoquinone in methanol.

The absence of structural change during the demethylation and oxidation was confirmed by reducing the quinones derived from (IV) and (V) with hydrogen and palladium to the corresponding quinols and methylation of the latter to give the starting compounds (IV and V; R = Me). The quinones derived from (IV) and (V) were insoluble in, and unaffected by, N-sulphuric acid at room temperature, but dissolved rather readily in N-sodium hydroxide to form dark solutions that gave resinous products on acidification.

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[10] Megson, " Phenolic Resin Chemistry," Butterworths Scientific Publns., London, 1958.

[11] Rodia and Freeman, *J. Org. Chem.*, 1959, **24**, 21.

[12] Jacini and Bachetti, *Gazzetta*, 1950, **80**, 760.

Electron interaction between π-electron systems linked by a saturated methylene bridge is known to occur in a number of organic compounds, and consequently it is reasonable to expect such an interaction to exist in the polymer chain segments described above. Interaction may arise as the result of the inductive or polarising influences of neighbouring groups or through electron delocalisation between the rings and adjoining methylene bridge owing to conjugative effects, especially hyperconjugation. Structural hyperconjugation will, however, depend on the possibility of free rotation of adjoining rings round the central methylene linkage. Further possible ring–ring interactions in the dimeric and trimeric chain segments can arise intramolecularly as a result of interspatial polarisation effects or (in the quinol forms) through hydrogen bonding to adjacent π-electrons[13] or carbonyl groups. Interaction between neighbouring π-electron systems such as exist in the polymer segments is likely to be reflected in their ultraviolet absorption spectra, and in the electrochemical behaviour of the polyquinone segments under aqueous and aprotic conditions.

The ultraviolet absorption spectra of the compounds described above have been examined for evidence of interaction of the π-electron systems *via* the saturated methylene linkage. Braude,[14] on the basis of deviations from additivity of the absorption intensities, and band shifts in the electronic spectra of molecules of the diphenylmethane and bibenzyl types, concluded that the saturated carbon atoms did not completely prevent interaction between the two rings. Spectral changes were even more marked with substituted bibenzyls.

The ultraviolet absorption spectrum of *p*-dimethoxybenzene (see Table 1) contained maxima at 226 and 289 mμ which are considered to correspond to the 200 and 260 mμ bands of benzene.[15] The insolubility of the higher members of the series in hydrocarbon solvents prevented observation of the behaviour of the 226 mμ band for the whole series.

TABLE 1.

Maxima of ultraviolet absorption bands.

Compound	$\lambda_{max.}$ (mμ) (Cyclohexane)	$10^{-3}\varepsilon$	Compound	$\lambda_{max.}$ (mμ) (Dichloromethane)	$10^{-3}\varepsilon$
1,4-Dimethoxybenzene	226	10·0	2-Methyl-*p*-benzoquinone	248	21·2
	289	3·4		~315	0·6
				434—435	0·03
1,4-Dimethoxy-2-methylbenzene	227	7·5	2,5-Dimethyl-*p*-benzoquinone	254	16·8
	289	3·25		315—316	0·2
				~422	0·02
1,4-Dimethoxy-2,5-dimethylbenzene	219	7·75	Diquinone from (IV)	252	35·4
	290	4·0		306	0·9
				~405	0·1
2,4-Dimethylphenol	279	2·1		413	0·1
	285·5	1·9		~422	0·1
1,4-Di(chloromethyl)-2,5-dimethoxybenzene	210	24·6	Triquinone from (V)	250	44·4
	235	8·75		301	1·4
	308	4·65		400—422	0·2
IV; R = Me	204	53·1	Quinone from (VI)	264	16·9
	292	9·5		~341	0·3
2,2′,5,5′-Tetramethoxy-4,4′-dimethylbibenzyl	203	72·1		~426	0·6
	292	7·3			
VII; R = Me	292 *	13·1			
V; R = Me	293 *	14·6			
VI; R = Me	288 *	9·0			

* In 4% dioxan in EtOH.

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[13] Beckering, *J. Phys. Chem.*, 1961, **65**, 206.

[14] Braude, *J.*, 1949, 1902.

[15] Albrecht and Simpson, *J. Chem. Phys.*, 1955, **23**, 1480.

However, substitution by two methyl groups, or by one methyl and a 2,5-dimethoxy-4-methylbenzyl group, in the nucleus appeared to displace the 226 mμ band to shorter wavelengths, with considerable intensification in the case of compound (IV). On the other hand, the 290 mμ band remained virtually unchanged in position throughout the series, but the higher members showed absorption intensities in excess of those expected from the summed values of the intensities of the relevant fragments. When the two rings were separated by an ethylene linkage the absorption intensity was reduced to approximately the additive value. These results suggest that hyperconjugative effects are very small or do not occur in these compounds since the usual red shift, arising from a decrease in the energy-level difference between the ground and the excited state, is not significantly present (see, *e.g.*, ref. 16). Changes in absorption intensity without shift of the band maxima observed in other series have been discussed for *m*-polyphenyls [17] and for the benzocycloalkenes.[18] Murrell [19] has also considered the influence of steric factors on absorption intensities in linked π-electron systems.

Molecular models of the compounds (IV and V) indicate that non-planar configurations will be favoured even in solution since such configurations permit maximum separation of the oxygen atoms, *i.e.*, their repulsive interaction will be minimised. However, the models show that rotation of the aromatic rings with respect to the methylene-carbon atom is possible, but since the motion of rotation is somewhat complicated (owing to steric hindrance) the period of rotation is likely to be large. These facts again suggest that hyperconjugation effects are likely to be small or absent.

The spectral characteristics of the polyquinone segments described above may now be considered. Of the three principal ultraviolet absorption bands of *p*-benzoquinone in solution at 250, 282, and ~410 mμ, the first two have been assigned to $\pi \longrightarrow \pi^*$ transitions and the third to a $n \longrightarrow \pi^*$ transition.[20] For compounds (V) and (VII) in dichloromethane there were small changes in the position of the three main bands compared with the simple monomeric quinones (see Table 1). The intensity of the 250 mμ band was close to the expected additive value, but on passage up the series the 315 mμ band of toluquinone was displaced towards lower wavelengths and was slightly intensified. Throughout the series the band around 420 mμ became gradually more diffuse, with submerged fine structure; the intensity of this band exceeded the additive value but, because of its broad nature, significant shifts of the nearly submerged peaks could not be measured precisely. The position of a band arising from a $n \longrightarrow \pi^*$ transition is known to be sensitive to environmental changes and the observed spectral changes in this region may arise through such causes. The much more distinct changes shown by the quinone from compound (VI) may similarly arise because of intramolecular hydrogen bonding.

The ultraviolet absorption spectra of the various chain segments and of the monomeric units suggest, therefore, that interaction occurs between two π-electron systems linked through a single saturated atom, but the exact nature of the interaction cannot be determined at present. The influence of ring–ring interactions on electrochemical behaviour is considered in the following paper.

EXPERIMENTAL

Microanalyses were carried out by the Microanalytical Section of this Laboratory. Ultraviolet absorption spectra were measured by means of a Unicam S.P. 500 spectrophotometer. Infrared absorption spectra of solids dispersed in potassium chloride discs were measured on a Grubb–Parsons G.S.3 double-beam grating instrument; only strong and medium bands are reported, these being correct to ±3 cm.$^{-1}$ except where indicated.

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[16] Coulson and Crawford, *J.*, 1953, 2050; Crawford, *J.*, 1953, 1061; Erdtman, Granath, and Schulz, *Acta Chem. Scand.*, 1954, **8**, 1442.

[17] Dewar, *J.*, 1952, 3544; Murrell and Longuet-Higgins, *J.*, 1955, 1552.

[18] Moor, Marcus, Fenton, and Arnold, *Tetrahedron*, 1959, **5**, 179.

[19] Murrell, *J.*, 1956, 3779.

[20] Orgel, *Trans. Faraday Soc.*, 1956, **52**, 1172.

1,4-*Di(chloromethyl)-2,5-dimethoxybenzene* (cf. ref. 21).—Finely powdered *p*-dimethoxybenzene (70 g.) was added portion-wise to a mixture of 40% formaldehyde solution (400 ml.) and concentrated hydrochloric acid (540 ml.) previously saturated with hydrogen chloride at 0°. The temperature was kept below 35° and stirring continued for 2 hr. after addition of the dimethoxybenzene. The solid product (78 g.), recovered in the usual way was recrystallised from benzene and then carbon tetrachloride, to give 1,4-di(chloromethyl)-2,5-dimethoxybenzene, m. p. 165° (Found: C, 51·1; H, 5·1; Cl, 29·9. Calc. for $C_{10}H_{12}Cl_2O_2$: C, 51·1; H, 5·1; Cl, 30·2%); $\nu_{max.}$ 2960, 2930, 2834, 1510, 1478, 1432, 1408, 1318, 1258, 1225, 1197, 1177, 1149, 1134, 1040, 911, 877, 832, 736, 677, and 605 cm.$^{-1}$.

Confirmation of the Orientation of 1,4-*Di(chloromethyl)-2,5-dimethoxybenzene.*—The chloromethyl compound (2·5 g.) in "AnalaR" ethyl acetate (200 ml.) was hydrogenated in the presence of Adams catalyst (200 mg.) and anhydrous potassium carbonate (500 mg.). Recovery of the product (2 g.) in the usual way and sublimation *in vacuo* and crystallisation from light petroleum (b. p. 60—80°) gave 1,4-dimethoxy-2,5-dimethylbenzene, m. p. 112° (lit.[12], 108°) (Found: C, 72·2; H, 9·1. Calc. for $C_{10}H_{14}O_2$: C, 72·3; H, 8·4%), $\nu_{max.}$ 3000, 2938, 2904, 2838, 2822, 1520, 1500, 1468, 1446, 1398, 1371, 1301, 1216, 1197, 1186, 1048, 996, 869, 826, and 692 cm.$^{-1}$. This product (800 mg.) was heated with pyridinium chloride (5 g.) at 200° for 4 hr. Working up in the usual way gave a product (500 mg.), m. p. 211—216°, which on recrystallisation from toluene gave 2,5-dimethylquinol as needles, m. p. 217° (lit., 217°) (Found: C, 69·5; H, 7·4. Calc. for $C_8H_{10}O_2$: C, 69·5; H, 7·3%).

1,4-*Di(acetoxymethyl)-2,5-dimethoxybenzene.*—This substance was prepared by refluxing 1,4-di(chloromethyl)-2,5-dimethoxybenzene (2·35 g.) and "AnalaR" anhydrous sodium acetate (1·70 g.) in glacial acetic acid (40 ml.) for 3 hr. and recrystallised from light petroleum (b. p. 80—100°) containing a little benzene as prisms, m. p. 122—123° (Found: C, 59·4; H, 6·3. $C_{14}H_{18}O_6$ requires C, 59·6; H, 6·4%), $\nu_{max.}$ 2956, 1730, 1515, 1470, 1418, 1386, 1371, 1360, 1320, 1242, 1216, 1182, 1040, 1022, 982, 960, 928, 899, 846, 696, 618, and 607 cm.$^{-1}$.

Reaction of 1,4-*Di(chloromethyl)-2,5-dimethoxybenzene with Acetic Acid.*—(i) A solution of 1,4-di(chloromethyl)-2,5-dimethoxybenzene (235 mg.) in glacial acetic acid (30 ml.) contained in a 150-ml. flask was refluxed under a slow stream of oxygen-free nitrogen. The liberated hydrogen chloride passed into a solution of silver nitrate in 1% nitric acid. After 7 hours' refluxing no more silver chloride was precipitated and the weight of the dry precipitate (0·2537 g.) corresponded to 1·77 mol. Removal of the acetic acid with addition of benzene gave a crystalline residue (280 mg.), m. p. 121—123°, shown to be 1,4-di(acetoxymethyl)-2,5-dimethoxybenzene by a mixed m. p. and the infrared absorption spectrum.

(ii) 1,4-Di(chloromethyl)-2,5-dimethoxybenzene (1·0 g.) was heated in glacial acetic acid (40 ml.) containing concentrated hydrochloric acid (2 ml.) for 22 hr. on the steam-bath (*ca.* 92°). Concentration of the solution gave crystals, m. p. 160—165° (550 mg.), which the infrared spectrum revealed as unchanged di(chloromethyl) compound. Removal of the rest of the acetic acid by addition of benzene and evaporation *in vacuo* gave a brown gum (470 mg.), the infrared spectrum of which indicated it to be a mixture of the di(acetoxymethyl) and di(chloromethyl) compounds.

1,4-*Di-(2-hydroxy-3,5-dimethylbenzyl)-2,5-dimethoxybenzene.*—After being kept at room temperature for 96 hr. a mixture of powdered 1,4-di(chloromethyl)-2,5-dimethoxybenzene (7·1 g.) and 2,4-dimethylphenol (25 g.) was triturated with light petroleum (b. p. 80—100°). The insoluble material recrystallised from light petroleum (b. p. 80—100°) containing 5% of benzene, to give 1,4-*di-(2-hydroxy-3,5-dimethylbenzyl)-2,5-dimethoxybenzene* (4·9 g.) as needles, m. p. 177—178° [Found C, 76·7; H, 7·6; MeO; 15·2%; *M* (Rast), 382. $C_{26}H_{30}O_4$ requires C, 76·8; H, 7·4; MeO, 15·3%; *M*, 406·5], $\nu_{max.}$ *ca.* 3355, 2933, 2907, 1504, 1488, 1460, 1405, 1348, 1250, 1222, 1203, 1155, 1032, 1017, 870, 855, 836, 766, 758, and 662 cm.$^{-1}$.

Treatment of the trinuclear compound with pyridine and acetic anhydride at room temperature afforded the *diacetate* which after recrystallisation from light petroleum (b. p. 80—100°)–benzene had m. p. 144—145° (Found: C, 73·4; H, 7·1. $C_{30}H_{34}O_6$ requires C, 73·5; H, 7·0%), $\nu_{max.}$ 2916, 1754, 1497, 1475, 1437, 1370, 1226, 1205, 1190, 1163, 1142, 1015, 933, 909, and 860 cm.$^{-1}$.

2,5-*Di-(2-hydroxy-3,5-dimethylbenzyl)quinol.*—1,4-Di-(2-hydroxy-3,5-dimethylbenzyl)-2,5-dimethoxybenzene (3·0 g.) was heated with pyridinium chloride (12·0 g.) at 180—200° for 3 hr.

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[21] B.P. 347,892/1931.

under nitrogen. Addition of deoxygenated water (10 ml.) to the cooled mixture precipitated a white solid (2·6 g.), m. p. 304—307° (decomp.). Recrystallisation of this from aqueous methanol gave 2,5-di-(2-hydroxy-3,5-dimethylbenzyl)quinol, m. p. 309° (decomp.) (lit.,[22] 292—294°) (Found: C, 76·3; H, 7·2. Calc. for $C_{24}H_{26}O_4$: C, 76·2; H, 6·9%). The *tetra-acetate* formed prisms (from ethyl acetate), m. p. 217—218° [Found: C, 70·4; H, 6·3%; *M* (Rast), 531. $C_{32}H_{34}O_8$ requires C, 70·3; H, 6·3%; *M*, 546·6], $\nu_{max.}$ *ca.* 3330, *ca.* 3240, 3010, 2934, 2903, 2862, 1495, 1488, 1445, 1429, 1372, 1360, 1317, 1309, 1277, 1214, 1183, 1160, 1032, 1012, 971, 960, 917, 877, 861, 833, 777, 760, 714, and 685 cm.$^{-1}$.

2,5-*Di*-(2-*hydroxy*-3,5-*dimethylbenzyl*)-1,4-*benzoquinone*.—2,5-Di-(2-hydroxy-3,5-dimethylbenzyl)quinol (1·0 g.), suspended in boiling methanol (125 ml.), was treated with solid *p*-benzoquinone (3 × 200 mg., at 10-min. intervals), and then refluxing was continued for an additional 10 min. On cooling, deep red crystals (580 mg.) separated out which recrystallised from ethanol, to give 2,5-*di*-(2-*hydroxy*-3,5-*dimethylbenzyl*)-1,4-*benzoquinone* as needles, m. p. 265° (decomp.; rapid heating) (Found: C, 76·5; H, 6·3. $C_{24}H_{24}O_4$ requires C, 76·6; H, 6·4%), $\nu_{max.}$ *ca.* 3397 3010, 2960, 2930, 2904, 2854, 1638, 1597, 1485, 1430, 1370, 1352, 1323, 1301, 1280, 1248, 1239, 1196, 1144, 1108, 1010, 973, 942, 917, 854, 811, 783, 760, 724, and 705 cm.$^{-1}$.

1,4-*Bis*-(2,5-*dimethoxybenzyl*)-2,5-*dimethoxybenzene*.—1,4-Di(chloromethyl)-2,5-dimethoxybenzene (4 g.) and *p*-dimethoxybenzene (40 g.) were heated at 190° under dry nitrogen until hydrogen chloride evolution ceased (3 hr.). After cooling, the melt was powdered and extracted with cold light petroleum (b. p. 80—100°). The residue was extracted with hot light petroleum (b. p. 100—120°) from which 1,4-*bis*-(2,5-*dimethoxybenzyl*)-2,5-*dimethoxybenzene* (3·4 g.) crystallised on cooling. Filtration of a 1 : 1 benzene–light petroleum (b. p. 60—80°) solution through alumina, and recrystallisation from light petroleum (b. p. 100—120°), provided a pure specimen, m. p. 157—158° [Found: C, 71·4; H, 6·9%; *M* (Rast), 420·5. $C_{26}H_{30}O_6$ requires C, 71·2; H, 6·9%; *M*, 438·5], $\nu_{max.}$ 2996, *ca.* 2950, 2938, 2917, 2834, 1612w, 1590, 1502, 1465, 1446, 1428, 1405, 1311, 1273, 1232, 1212, 1188, 1150, 1124, 1050, 1030, 935, 915, 880, 865, 832, 800, 711, and 643 cm.$^{-1}$.

2,5-*Bis*-(2,5-*dihydroxybenzyl*)*quinol*.—1,4-Bis-(2,5-dimethoxybenzyl)-2,5-dimethoxybenzene was treated with anhydrous pyridinium chloride as previously described. The *quinol* (150 mg.) was crystallised from aqueous ethanol, recovered by centrifuging the solution, and recrystallised from aqueous ethanol as a pale buff-coloured powder, m. p. 190° (rapid heating) (Found: C, 67·5; H, 5·4. $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1%), which readily darkened on exposure to air. The derived *hexa-acetate* had m. p. 236—237° (from ethyl acetate) (Found: C, 63·4; H, 5·3. $C_{32}H_{30}O_{12}$ requires C, 63·4; H, 5·0%).

1,4-*Bis*-(2,5-*dimethoxy*-4-*methylbenzyl*)-2,5-*dimethoxybenzene*.—(i) 1,4-Di(chloromethyl)-2,5-dimethoxybenzene (4·5 g.) and 1,4-dimethoxy-2-methylbenzene (13 g.) to which 2 drops of 2N-sulphuric acid had been added were heated at 120—140° for 50 min. under nitrogen. Evolution of hydrogen chloride occurred at 120° but ceased after 50 min. and the required trimer separated from the solution. After cooling, the product was triturated with cold light petroleum (b. p. 80—100°) (50 ml.), and the insoluble trimer removed by filtration. Crystallisation from 1 : 2 benzene–light petroleum (b. p. 80—100°) (450 ml.) furnished 1,4-*bis*-(2,5-*dimethoxy*-4-*methylbenzyl*)-2,5-*dimethoxybenzene* (5·1 g.) as needles, which on purification by filtration in the same solvent mixture through alumina had m. p. 196·5—197° [Found: C, 71·8; H, 7·3%; *M* (Rast), 465. $C_{28}H_{34}O_6$ requires C, 72·1; H, 7·35%; *M*, 466·6], $\nu_{max.}$ 2985, 2950, 2908, 2904, 2825, 1512, 1478, 1432, 1403, 1374, 1312, 1290, 1212, 1175, 1047, 1003, 934, 876, 869, 854, 847, 772, and 665 cm.$^{-1}$.

(ii) A mixture of 2,5-dimethoxy-4-methylbenzyl chloride (2·0 g.) and 1,4-dimethoxybenzene (2·74 g.) was heated at 100° for 4 hr. under nitrogen. The solid product was recrystallised successively from benzene and benzene–light petroleum (b. p. 80—100°), to give 1,4-bis-(2,5-dimethoxy-4-methylbenzyl)-2,5-dimethoxybenzene (1·3 g.), m. p. 195°, undepressed on admixture with the compound prepared under (i) and possessing a similar infrared absorption spectrum (Found: C, 72·1; H, 7·4%).

2,5-*Bis*-(2,5-*dihydroxy*-4-*methylbenzyl*)*quinol*.—Demethylation of the preceding compound by pyridinium chloride gave the *hexahydroxy-compound* m. p. 317—318° (Found: C, 69·0; H, 6·0. $C_{22}H_{22}O_6$ requires C, 69·1; H, 5·8%), $\nu_{max.}$ *ca.* 3185, *ca* 3020, 2920, 2858, 1515, 1435, 1376, 1340, 1186, 1002, 926, 879, and 702 cm.$^{-1}$. The *hexa-acetate* formed needles (from ethyl

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[22] von Euler, Adler, de Kispeczy, and Fagerlund, *Arkiv Kemi, Min., Geol.*, 1940, **14**, *A*, No. 10.

acetate), m. p. 216—217° (Found: C, 64·4; H, 5·5; Ac, 39·9, 41·6. $C_{34}H_{34}O_{12}$ requires C, 64·4, H, 5·4; Ac, 40·7%), $\nu_{max.}$ 1761, 1502, 1433, 1407, 1370, 1212, 1186, 1155, 1042, 1012, 943, 920, 910, and 592 cm.$^{-1}$.

2,5-Di-(5-methyl-1,4-benzoquinonylmethyl)-1,4-benzoquinone.—2,5-Bis-(2,5-dihydroxy-4-methylbenzyl)quinol (600 mg.) in boiling methanol (150 ml.) was oxidised by *p*-benzoquinone (550 mg.) as described above. On cooling, orange needles (320 mg.) separated. Chromatography in benzene on silica gel furnished the *triquinone* as yellow needles (260 mg.), m. p. 188° (decomp.) (Found: C, 70·3; H, 4·5. $C_{22}H_{16}O_6$ requires C, 70·2; H, 4·3%), $\nu_{max.}$ 1640, 1609, 1433, 1412, 1374, 1350, 1292, 1250, 1150, 1000, 950, 928, 918, 840, 730, 680, and 651 cm.$^{-1}$. Hydrogenation over palladised charcoal gave 2,5-bis-(2,5-dihydroxy-4-methylbenzyl)quinol, m. p. 315—316°, comparable (mixed m. p., infrared absorption spectrum, and analysis) with the compound obtained previously. Acetylation of the reduction product yielded the expected hexa-acetate. The hexahydroxy-compound with diazomethane gave 1,4-bis-(2,5-dimethoxy-4-methylbenzyl)-2,5-dimethoxybenzene, m. p., mixed m. p., and infrared absorption spectrum identical with those of the compound described above.

2,2′,5,5′-Tetramethoxy-4,4′-dimethyldiphenylmethane.—1,4-Dimethoxy-2-methylbenzene (5 g.), 35% formaldehyde solution (5 ml.), and concentrated hydrochloric acid (5 ml.) were warmed at about 75° for 4 hr. and then set aside for 16 hr. at room temperature. The product (2·2 g.) was deposited as a white solid which after filtration and washing with water crystallised from 95% ethanol. Recrystallisation from ethanol gave 2,2′,5,5′-tetramethoxy-4,4′-dimethyldiphenylmethane [12] as needles, m. p. 147—147·5° [Found: C, 71·9; H, 7·65%; *M* (Rast), 314. Calc. for $C_{19}H_{24}O_4$: C, 72·1; H, 7·65%; *M*, 316], $\nu_{max.}$ 2994, 2955, 2933, *ca.* 2907, 2833, 1506, 1458, 1399, 1372, 1316, 1302, 1208, 1175, 1044, 1002, 935, *ca.* 870, 855, 841, 775, and 662 cm.$^{-1}$.

2,2′,5,5′-Tetrahydroxy-4,4′-dimethyldiphenylmethane was prepared by demethylation of this ether with pyridinium chloride and after recrystallising from acetic acid had m. p. 286—287° (decomp.) (Found: C, 69·0; H, 6·4. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2%) {tetra-acetate, m. p. 162—163° [from benzene–light petroleum (b. p. 80—100°)] (Found: C, 64·5; H, 5·85. $C_{23}H_{24}O_8$ requires C, 64·5; H, 5·65%)}, $\nu_{max.}$ *ca.* 3215, *ca.* 3140, 2916, *ca.* 1517, 1433, 1266, 1185, *ca.* 1155, 1002, 926, 872, 859, 831, 776, 701, and 581 cm.$^{-1}$.

2-Methyl-5-(5-methyl-1,4-benzoquinonylmethyl)-1,4 benzoquinone.—Oxidation of 2,2′,5,5′-tetrahydroxy-4,4′-dimethyldiphenylmethane (1·0 g.) in boiling methanol (50 ml.) by *p*-benzoquinone (830 mg.) gave orange needles, m. p. 148—152°. Recrystallisation from benzene–light petroleum (b. p. 80—100°) followed by chromatography on silica gel gave coloured eluates (benzene) from which were recovered the pure *diquinone* (360 mg.), m. p. 158° (decomp.) [from benzene–light petroleum (b. p. 80—100°)] (Found: C, 70·2; H, 4·9. $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7%), $\nu_{max.}$ 1649, 1611, 1433, 1416, 1374, 1350, 1289, 1251, 1205, 1186, 1138, 1042, 1006, 953. 925, 833, 796, 788, 725, 683, 662, and 650 cm.$^{-1}$. Hydrogenation over palladised charcoal gave 2,2′,5,5′-tetrahydroxy-4,4′-dimethyldiphenylmethane, m. p. 286—287 (decomp.) (from methanol, then acetic acid), identical in mixed m. p., infrared absorption, and analysis with the compound obtained as above. The tetrahydroxy-compound (300 mg.) was treated in methanol (25 ml.) with diazomethane in methanol (25 ml.), to give 2,2′,5,5′-tetramethoxy-4,4′-dimethyldiphenylmethane (260 mg.), m. p., mixed m. p., and infrared absorption spectrum as for the compound described above.

Preparation of Poly-(2,5-dimethoxy-1,4-phenylenemethylene).—1,4-Di(chloromethyl)-2,5-dimethoxybenzene (11·8 g.) and *p*-dimethoxybenzene (6·9 g.) were heated in glacial acetic acid (75 ml.) on the steam bath for 24 hr. The polycondensation product was precipitated as a pale cream granular solid which after being washed with acetic acid and water was dried (13·9 g.) and analysed (polymer A) [Found: C, 72·1; H, 7·0; Cl, 0·0. Calc. for $(C_9H_{10}O_2)_n$: C, 72·0; H, 6·7%], $\nu_{max.}$ 2982, 2920, 2822, 1506, 1473, 1430, 1398, 1323, 1306, 1210, 1172, 1120, 1042, 990, 925, 854, and 658 cm.$^{-1}$.

The dry polymer (39·1 g.) was extracted by boiling solvents (Soxhlet) to give the fractions listed in Table 2.

Polycondensation Product from 1,4-Di(chloromethyl)-2,5-dimethoxybenzene and Quinol.—The chloromethyl compound (9·4 g.) and quinol (4·4 g.) were heated in glacial acetic acid (60 ml.) on the steam-bath for 24 hr. The buff-coloured insoluble polymer was removed by filtration and washed successively with acetic acid, water, N-sodium hydroxide, water, 2N-hydrochloric acid, and finally with water until the washings were neutral. The air-dried polymer (Polymer B) weighed 18 g. and contained 50% of water. A sample dried at 105° [Found:

C, 69·0; H, 6·1. Calc. for $(C_{16}H_{16}O_4)_n$: C, 70·6; H, 5·9%] had $\nu_{max.}$ *ca.* 3390, 2982, 2920, 2826, 1654, 1610, 1505, 1463, 1457, 1420, 1402, 1318, 1290, 1214, 1177, 1155, 1038, 987, 936, 907, 860, and 690 cm.$^{-1}$.

Polycondensation Product from 1,4-*Di*(*chloromethyl*)-2,5-*dimethoxybenzene and Quinol Diacetate*.—A solution of the chloromethyl compound (11·8 g.) and quinol diacetate (9·7 g.) in glacial acetic acid (75 ml.) was refluxed for 24 hr. The insoluble polycondensation product was removed by filtration and washed with acetic acid and with water to neutrality. The air-dried polymer (Polymer C) (10·7 g.) contained 10% of water. The analytical sample was dried at 80° in a vacuum [Found: C, 69·8; H, 5·2. Calc. for $(C_{16}H_{16}O_4)_n$: C, 70·6; H, 5·9%. Calc. for $(C_{20}H_{20}O_6)_n$: C, 67·4; H, 5·7%] and had $\nu_{max.}$ *ca.* 3390, 2982, 2930, 2836, 1753, 1646, 1610, 1503, 1463, 1426, 1397, 1367, 1335, 1280, 1213, 1179, 1157, 1118, 1100, 1040, 986, *ca.* 970, 909, 862, and 666 cm.$^{-1}$.

TABLE 2.

		Weight			Found (%)	
		g.	%	M. p.	C	H
A1	Polymer insoluble in boiling $NMe_2{\cdot}CHO$	29·8	76·2	—	72·1	6·7
A2	Polymer soluble in boiling $NMe_2{\cdot}CHO$	9·3	23·8	244—247°	71·9	6·6
A3	Fraction of A2 polymer soluble in boiling C_6H_6	1·6	4·1	223—226°	72·3	6·7

Demethylation of Polymers.—Polymers A, B, and C were refluxed with an excess of pyridinium chloride or with 55% hydriodic acid (freshly distilled from red phosphorus) under nitrogen. In the latter instance the methyl iodide liberated was collected in a Dean and Stark apparatus and measured. The extent of demethylation was also assessed from the intensity of the methoxyl band at 1040 cm.$^{-1}$. Almost quantitative demethylation occurred. The experimental data are in Table 3.

In each case the demethylated polymer was washed successively with water, 2N-hydrochloric acid, water, N-sodium hydroxide, water, 2N-hydrochloric acid, and then water until the eluate was neutral. The polyquinol was oxidised to the polyquinone by acidic ferric ammonium sulphate solution or by refluxing ethanolic benzoquinone (5 hr.), as was confirmed by the infrared absorption of the products.

TABLE 3.

		Methyl iodide (g.)		Found (%)	
Polymer	Reagent	Theor.	Collected	C	H
A	HI	4·0 g.	4·3 g.	68·85	4·8
A	$[C_5H_6N]Cl$	—	—	69·5	4·9
B	,,	—	—	69·4	3·93
C	HI	8·0	6·0	70·0	4·3
		Calc. for $(C_7H_6O_2)_n$		68·8	4·95
		,, $(C_7H_4O_2)_n$		70·0	3·4

Quinol–Phenol–Formaldehyde Polymer.—This was prepared [9] by using a 1 : 1 : 3 molar ratio. The resin was sieved wet into two fractions: (i) passing a BSS standard sieve No. 16 but retained by a BSS standard sieve No. 30; and (ii) passing a BSS standard sieve No. 30 but retained by BSS standard sieve No. 60. The polymers were oxidised to the polyquinones by the methods described.

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